Family list
3 application(s) for: **JP2002237480 (A)**
Sorting criteria: Priority Date Inventor Applicant Ecla

1. **MANUFACTURING METHOD AND DEVICE OF SEMICONDUCTOR ELEMENT**
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   EC: **IPC:** ***H05H1/46; B01J19/08; C23C16/503;*** (+18)
   Publication info: **JP2002237463 (A)** - 2002-08-23 **Priority Date:** 2000-07-28

2. **METHOD OF TREATING BASE MATERIAL WITH DISCHARGE PLASMA**
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   EC: **IPC:** ***H05H1/26; B01J19/08; H01L21/205;*** (+14)
   Publication info: **JP2002237480 (A)** - 2002-08-23 **Priority Date:** 2000-07-28

3. **DISCHARGE PLASMA PROCESSING APPARATUS**
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   EC: **IPC:** ***H05H1/24; C23C16/50; H01L21/205;*** (+8)
   Publication info: **JP2005347278 (A)** - 2005-12-15 **Priority Date:** 2000-07-28

(19) Japanese Patent Office (JP)
(12) Publication of Laid-Open Patent Application (A)
(11) Publication Number of Patent Application:
Japanese Patent Laid-Open Publication No. 2002-237480
(P2002-237480A)
(43) Publication Date of Application: August 23, 2002
(51) Int. Cl.^{7}: H01L 21/304, B01J 19/08, H01L 21/205, 21/3065, H05H 1/26
Identification Mark: 645
FI: H01L 21/304, B01J 19/08, H01L 21/205, H05H 1/26, 1/46
645C, H, M
Theme Code (reference): 4G075, 5F004, 5F045
Request for Examination: Not requested
Number of Claims: 14
OL
Total 12 pages
Continued to the last page
(21) Application Number:
Japanese Patent Application No. 2001-200835 (P2001-200835)
(22) Date of Filing: July 2, 2001
(31) Priority Application Number:
Japanese Patent Application No. 2000-229322 (P2000-229322)
(32) Priority Date: July 28, 2000
(33) Priority Country: Japan (JP)
(31) Priority Application Number:
Japanese Patent Application No. 2000-369489 (P2000-369489)
(32) Priority Date: December 5, 2000
(33) Priority Country: Japan (JP)
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Continued to the last page
(54) [Title of the Invention]
Discharge Plasma Treatment Method
(57) [Abstract]
[Problem to be Solved] To provide an atmospheric pressure plasma treatment method which can treat a large-area base material, capable of a uniform and high speed treatment, and furthermore, does not damage the base material.
[Means for Solving the Problem] A discharge plasma treatment method in which a solid dielectric is set on the opposing surface of at least one of the electrodes opposing to each other, under a pressure in the vicinity of atmospheric pressure, and discharge plasma obtained by introducing a treatment gas between the electrodes and applying a pulsed electric field is induced to a base material to be treated, which is placed outside the discharge space, so as to have contact with the base material to be treated. By adopting this method, a large-area base material can be treated easily, and an electric and thermal burden to the base material to be treated during the treatment can be decreased.
[Scope of Claims]
[Claim 1] A discharge plasma treatment method wherein a solid dielectric is set on an opposing surface of at least one of electrodes opposing to each other, under a pressure in the vicinity of atmospheric pressure, and discharge plasma obtained by introducing a treatment gas between the electrodes and applying a pulsed electric field is induced to a base material to be treated, which is placed outside a discharge space, so as to have contact with the base material to be treated.
[Claim 2] A discharge plasma treatment method according to claim 1, wherein the opposing electrodes are parallel plate electrodes.
[Claim 3] A discharge plasma treatment method according to claim 1 or 2, wherein the opposing electrodes are a combination of parallel plate electrodes in a plurality of groups.
[Claim 4] A discharge plasma treatment method according to claim 1, wherein the opposing electrodes are roll electrodes.
[Claim 5] A discharge plasma treatment method according to claim 1, wherein the opposing electrodes are a combination of opposing parallel plate electrodes and opposing roll electrodes.
[Claim 6] A discharge plasma treatment method according to any one of claims 1 to 5,

wherein a guide is provided roughly vertically from a plasma outlet of plasma generated by the opposing electrodes toward a base material to be treated.

[Claim 7] A discharge plasma treatment method according to any one of claims 1 to 6, wherein the plasma outlet of the plasma generated by the opposing electrodes is 50 mm or more on a side.

[Claim 8] A discharge plasma treatment method according to any one of claims 1 to 7, wherein surface roughness of the electrodes and/or the solid dielectric is 10 μm or less.

[Claim 9] A discharge plasma treatment method according to any one of claims 1 to 8, wherein a temperature of the base material to be treated is 120 °C or less.

[Claim 10] A discharge plasma treatment method according to any one of claims 1 to 9, wherein pulse rise and/or fall time of the pulsed electric field is 10 μs or less.

[Claim 11] A discharge plasma treatment method according to any one of claims 1 to 10, wherein field intensity of the pulsed electric field is in a range of 10 to 1000 kV/cm.

[Claim 12] A discharge plasma treatment method according to any one of claims 1 to 11, wherein, when plasma is brought into contact with the base material to be treated, a preliminary discharge is performed until a discharge condition becomes stable, and after that plasma is brought into contact with the base material to be treated.

[Claim 13] A discharge plasma treatment method according to claim 12, having a nozzle body standby mechanism which moves a gas outlet nozzle to over a base material surface after the preliminary discharge.

[Claim 14] A discharge plasma treatment method according to any one of claims 1 to 13, wherein a treatment to the base material to be treated is performed so that the both front and rear surfaces of the base material to be treated are treated at the same time by plasma from a plurality of opposing electrodes.

[0001]

[Technical Field of the Invention] The present invention relates to an atmospheric pressure plasma treatment method under a pressure in the vicinity of atmospheric pressure, especially a method for treating a substance to be treated, which is located away from a discharge space, with atmospheric pressure plasma.

[0002]

[Prior Art] Conventionally, a method in which surface reformulation of a substance to be treated or thin film formation on a substance to be treated is performed by generating glow discharge plasma under a low pressure condition has been put to practical use. However, such a treatment under a low pressure condition needs a vacuum chamber, a vacuum exhauster and the like, so that a surface treatment device becomes expensive and it has been hardly used when treating a large-area substrate or the like. Therefore,

a method for generating discharge plasma under a pressure in the vicinity of atmospheric pressure has been proposed.

[0003] As a conventional atmospheric pressure plasma treatment method, a method in which a treatment is performed under a helium atmosphere is disclosed in Japanese Patent Laid-Open Publication No. 2-48626, and a method in which a treatment is performed under an atmosphere of argon and acetone and/or helium is disclosed in Japanese Patent Laid-Open Publication No. 4-74525. However, the above-described methods all generate plasma in a gas atmosphere including an organic compound such as helium and acetone, so that the gas atmosphere is limited. In addition, helium is expensive, which is industrially disadvantageous. In the case where an organic compound is included, the organic compound itself often reacts with a substance to be treated, so that a desired surface reformulation treatment cannot be performed sometimes.

[0004] In addition, with a common atmospheric pressure plasma treatment method, a method in which a substance to be treated is set between parallel plate electrodes coated with a solid dielectric or the like, a treatment gas is introduced into a treatment chamber, a voltage is applied between the electrodes, and the substance to be treated is treated by the generated plasma mainly inside the treatment chamber is adopted, as described in Japanese Patent Laid-Open Publication No. 6-2149, Japanese Patent Laid-Open Publication No. 7-85997 and the like. When a method like this is used, the whole substance to be treated is placed in a discharge space, and the substance to be treated tends to be damaged, which has been a problem.

[0005] In order to solve the problem, a gun-type plasma treatment device having a plasma gas outlet on the edge has been developed, as a device which can easily perform a plasma treatment only to a specific part of a substance to be treated and can treat the substance to be treated continuously. For example, in Japanese Patent Laid-Open Publication No. 11-251304 and Japanese Patent Laid-Open Publication No. 11-260597, a plasma treatment device provided with a tubular reaction tube provided with an outside electrode and an inside electrode in the reaction tube, having a cooling mechanism for the both electrodes, which generates a glow discharge inside the reaction tube, and sprays plasma jet spewed from the reaction tube to a substance to be treated is disclosed. However, the above-described device uses plasma generated by an alternate current, so a process of cooling down things with rising temperature has to be included, which decreases efficiency, and the method still has a problem that a streamer discharge easily occurs. In addition, since the outlet is small, it takes a long time to perform a large-area treatment, and it is hard to perform a uniform treatment.

[0006]
[Problems to be Solved by the Invention] In view of the above-described problems, the object of the present invention is to provide an atmospheric pressure plasma treatment method which can deal with a high speed treatment and a large-area treatment, and does not damage a base material.
[0007]
[Means for Solving the Problems] The present inventors studied diligently to solve the above-described problems, and as a result, found out that a treatment capable of a uniform and high speed treatment and that does not damage a base material can be performed by bringing plasma generated under an atmospheric pressure condition, using a pulsed electric field, into contact with a base material to be treated placed outside a discharge space, then completed the invention.
[0008] That is, the first invention of the present invention is a discharge plasma treatment method wherein a solid dielectric is set on an opposing surface of at least one of electrodes opposing to each other, under a pressure in the vicinity of atmospheric pressure, and discharge plasma obtained by introducing a treatment gas between the electrodes and applying a pulsed electric field is induced to a base material to be treated, which is placed outside a discharge space, so as to have contact with the base material to be treated.
[0009] The second invention of the present invention is a discharge plasma treatment method according to claim 1, wherein the opposing electrodes are parallel plate electrodes.
[0010] The third invention of the present invention is a discharge plasma treatment method according to claim 1 or 2, wherein the opposing electrodes are a combination of parallel plate electrodes in a plurality of groups.
[0011] The fourth invention of the present invention is a discharge plasma treatment method according to claim 1, wherein the opposing electrodes are roll electrodes.
[0012] The fifth invention of the present invention is a discharge plasma treatment method according to claim 1, wherein the opposing electrodes are a combination of opposing parallel plate electrodes and opposing roll electrodes.
[0013] The sixth invention of the present invention is a discharge plasma treatment method according to any one of claims 1 to 5, wherein a guide is provided roughly vertically from a plasma outlet of plasma generated by the opposing electrodes toward a base material to be treated.
[0014] The seventh invention of the present invention is a discharge plasma treatment method according to any one of claims 1 to 6, wherein the plasma outlet of the plasma

generated by the opposing electrodes is 50 mm or more on a side.

[0015] The eighth invention of the present invention is a discharge plasma treatment method according to any one of claims 1 to 7, wherein surface roughness of the electrodes and/or the solid dielectric is 10 μm or less.

[0016] The ninth invention of the present invention is a discharge plasma treatment method according to any one of claims 1 to 8, wherein a temperature of the base material to be treated is 120 °C or less.

[0017] The tenth invention of the present invention is a discharge plasma treatment method according to any one of claims 1 to 9, wherein pulse rise and/or fall time of the pulsed electric field is 10 μs or less.

[0018] The eleventh invention of the present invention is a discharge plasma treatment method according to any one of claims 1 to 10, wherein field intensity of the pulsed electric field is in a range of 10 to 1000 kV/cm.

[0019] The twelfth invention of the present invention is a discharge plasma treatment method according to any one of claims 1 to 11, wherein, when plasma is brought into contact with the base material to be treated, a preliminary discharge is performed until a discharge condition becomes stable, and after that plasma is brought into contact with the base material to be treated.

[0020] The thirteenth invention of the present invention is a discharge plasma treatment method according to claim 12, having a nozzle body standby mechanism which moves a gas outlet nozzle to over a base material surface after the preliminary discharge.

[0021] The fourteenth invention of the present invention is a discharge plasma treatment method according to any one of claims 1 to 13, wherein a treatment to the base material to be treated is performed so that the both front and rear surfaces of the base material to be treated are treated at the same time by plasma from a plurality of opposing electrodes.

[0022]

[Embodiment Mode] The present invention is a discharge plasma method in which a solid dielectric is set on the opposing surface of at least one of the electrodes opposing to each other, under a pressure in the vicinity of atmospheric pressure, and discharge plasma obtained by introducing a treatment gas between the electrodes and applying a pulsed electric field between the electrodes is induced to a base material to be treated, which is placed in a position away from the discharge space, so as to have contact with the base material to be treated, and the treatment is performed. Hereinafter, the invention will be described in detail.

[0023] "Under a pressure in the vicinity of atmospheric pressure" described above means under a pressure in a range of 1.333×10^4 to 10.664×10^4 Pa. Especially, a range of 9.331×10^4 to 10.397×10^4 Pa where pressure control is easy and the device can be simple is preferable.

[0024] It is known that a plasma discharge condition is not maintained stably and the transfer to an arc discharge condition occurs quickly with gases other than specific gases such as helium and ketone, under a pressure in the vicinity of atmospheric pressure. However, it is believed that, by applying a pulsed electric field, a cycle in which the discharge is stopped before the transfer to an arc discharge occurs and the discharge is restarted is realized.

[0025] Under a pressure in the vicinity of atmospheric pressure, it is possible that discharge plasma is generated stably in an atmosphere which does not include a component that the time before a plasma discharge condition changes into an arc discharge condition is long such as helium, only when the method of the invention in which a pulsed electric field is applied is used.

[0026] According to the present invention, glow discharge plasma can be generated no matter what kind of gas exists in the plasma generation space. Not only with a plasma treatment under a known low pressure condition but also with an atmospheric pressure plasma treatment under a particular gas atmosphere, it is necessary to perform the treatment in a closed vessel sealed from outside air. However, according to the glow discharge plasma treatment method of the invention, a treatment with an open system, or with a low airtight system which prevents the gas from outflowing freely becomes possible.

[0027] Furthermore, a high-density plasma condition can be realized by a treatment under an atmospheric pressure, which is highly significant in performing a manufacture process of a semiconductor element such as a consecutive processing. For realizing the above-described high-density plasma condition, two functions which the invention has are related.

[0028] First, a function that gas molecules existing in the plasma generation space are excited effectively by applying a pulsed electric field having precipitous rise whose filed intensity is in a range of 0.5 to 250 kV/cm and rise time is 100 μm or less is one of them. Applying a pulsed electric field with slow rise is equivalent to putting energy with different sizes in a phased manner, and molecules which are ionized with low energy, that is, molecules with small first ionizing potential, are excited preferentially first, and next, when higher energy is put, molecules which have been already ionized are excited to a higher level, so that it is difficult to ionize molecules existing in the

plasma generation space effectively. On the other hand, according to a pulsed electric field whose rise time is 100 μm or less, energy is given to molecules existing in the space simultaneously, so the absolute number of molecules in an ionized-condition in the space is large, which means the plasma density is high.

[0029] Second, a function that molecules having more electrons than helium, that is, molecules with higher molecular weight than helium are selected as the ambient gas since plasma of a gas atmosphere other than helium can be obtained stably, and as a result, a space with a high electron density is realized. Generally, molecules having more electrons are ionized more easily. As described above, helium is a component which is not ionized easily, but after once ionized, it does not reach arc and exists for a long time in a glow plasma condition, therefore it has been used as an ambient gas for atmospheric pressure plasma. However, as long as the discharge condition is prevented from changing into arc, molecules with larger mass number which are ionized easily are used so that the absolute number of molecules in an ionized-condition in the space can be large and the plasma density can be heightened. With a prior art, it is impossible to generate glow discharge plasma except under an atmosphere where helium exists 90 % or more. Only Japanese Patent Laid-Open Publication No. 4-74525 discloses a technique in which a discharge is performed by sin wave in an atmosphere made of argon and acetone. However, according to the present inventor's additional test, a stable and high-speed treatment cannot be performed at a practical level. In addition, since the atmosphere contains acetone, a treatment except hydrophilic object is disadvantageous.

[0030] As described above, the present invention enables a stable glow discharge under an atmosphere where molecules having more electrons than helium exist excessively, more specifically, under an atmosphere containing compounds with 10 or more of molecular weight at a rate of 10 volume % or more, for the first time, and by this, a high-density plasma condition advantageous for a surface treatment is realized.

[0031] A treatment gas used for the invention is not limited specially, as long as it is a gas which generates plasma by applying an electric field, preferably a pulsed electric field, and various gases can be used according to the treatment object.

[0032] As a material gas as a material for a thin film, for example, a silane-containing gas such as SiH_4, Si_2H_6, $SiCl_4$, SiH_2Cl_2 and $Si(CH_3)_4$ forms an amorphous silicon film and a polysilicon film. And, an SiN film is formed from the above-described silane-containing gas and a nitrogen-containing gas such as anhydrous ammonia and a nitrogen gas, and an SiON film is formed from the above-described silane-containing gas, the above-described nitrogen-containing gas and an oxygen-containing gas such as

O_2 and O_3, respectively.

[0033] Furthermore, an oxide film such as SiO_2 is obtained from a silane-containing gas such as SiH_4, Si_2H_6 and tetraethoxysilane and an oxygen gas.

[0034] Furthermore, a metal thin film such as Al, In, Mo, W and Cu or a metal silicide thin film such as $TiSi_2$ and WSi_2 can be formed from a mixed gas of $Al(CH_3)_3$, $In(C_2H_5)_3$, $MoCl_6$, WF_6, $Cu(HFAcAc)_2$, $TiCl_6$ and the like, or a silane gas such as SiH_4.

[0035] Furthermore, a transparent conductive film such as In_2O_3+Sn, SnO_2+Sb and ZnO+Al is formed from $In(Oi{-}C_3H_7)_3$, $Zn(OC_2H_5)_2$, $In(CH_3)_3$, $Zn(C_2H_5)_2$ and the like.

[0036] Furthermore, a BN film is formed from B_2H_6, BCl_3, an NH_3 gas and the like, an SiOF film is formed from an SiF_4 gas, an oxygen gas and the like, and a polymer film and the like is formed from $HSi(OR)_3$, $CH_3Si(OR)_3$, $(CH_3)_2Si(OR)_2$ and the like.

[0037] Furthermore, an oxide film and the like such as Ta_2O_5, Y_2O_3, HfO_2 and ZnO_2 is formed from $Ta(OC_2H_5)_5$, $Y(OiC_3H_7)_3$, $Y(C_2H_5)_3$ $Hf(OiC_3H_7)_4$, $Zn(C_2H_5)_2$ and the like.

[0038] Furthermore, a DLC film can be formed from a carbon-containing gas such as CO_2, CH_4 and C_2H_5OH.

[0039] Furthermore, a fluorine-containing compound gas such as CF_4, C_2F_6, CF_3CFCF_2 and C_4F_8, an oxygen-containing compound gas such as O_2, O_3, H_2O, CH_3OH, C_2H_5OH, a nitrogen-containing compound gas such as N_2 and NH_3, a sulfur-containing compound gas such as SO_2 and SO_3, a polymerizable hydrophilic monomer gas such as acrylic acid, methacrylamide, polyethylene glycol dimethacrylate ester, and the like can be used according to the respective object.

[0040] Furthermore, an etching treatment and a dicing treatment can be performed using a halogen-series gas, an ashing treatment, a resist treatment and removal of organic matter contamination can be performed using an oxygen-series gas, and surface cleaning and surface reformulation can be performed using plasma by an inert gas such as argon and nitrogen.

[0041] In the invention, the above-described material gas may be used as a treatment gas directly, or may be diluted by a dilution gas and used as a treatment gas from a standpoint of economy, safety and the like. As the dilution gas, a noble gas such as neon, argon and xenon, or a nitrogen gas and the like may be used. They can be used separately, or two or more kinds of them may be mixed and used. Conventionally, a treatment under a pressure in the vicinity of atmospheric pressure is performed in the presence of helium. However, according to the method of the invention in which an electric field, preferably a pulsed electric field, is applied, a stable treatment in an argon or nitrogen gas which is less expensive than helium is possible, as described above.

[0042] Conventionally, under a pressure in the vicinity of atmospheric pressure, a

treatment is performed under an atmosphere where helium exists excessively. However, according to the method of the invention, a stable treatment in a gas such as argon and nitrogen which are less expensive than helium is possible. Furthermore, by performing the treatment in the presence of such gases with high molecular weight, having more electrons, a high-density plasma condition is realized and the treatment speed can be increased, which provides great industrial advantages.

[0043] The mixing ratio of a material gas and a dilution gas is decided arbitrarily by the kind of the dilution gas used. The concentration of a material gas is preferably in a range of 0.01 to 10 volume % in a treatment gas, and more preferably in a range of 0.1 to 10 volume %.

[0044] As the above-described electrodes, ones formed of a metal such as copper and aluminum, an alloy such as stainless and brass, an intermetallic compound and the like can be used. The shape of the electrode is not specially limited, but a structure with which the distance between opposing electrodes is constant is preferable, to prevent generation of an arc discharge due to electric field concentration. A parallel plate type, a cylindrical type, a cylindrical opposing plate type, a spherical opposing plate type, hyperbolic opposing plate type, a coaxial cylindrical structure and the like, and combination of two or more kinds from these, for example, can be cited as an electrode structure which meets the condition.

[0045] In addition, besides the roughly certain structures, a cylinder opposing cylindrical type with large cylinder curvature can be used as an opposing electrode, since degree of electric field concentration which causes an arc discharge is low. The curvature is preferably at least radius 20 mm or more. Although it depends also on the dielectric constant of a solid dielectric, with a curvature less than that, an arc discharge due to electric field concentration is easily concentrated. When each curvature is radius 20 mm or more, it is all right that the curvatures of the opposing electrodes are different. The larger the curvature is, the closer to plates approximately, and the more stable discharge is obtained. So it is more preferable that the curvature is radius 40 mm or more.

[0046] Furthermore, as for the electrodes for generating plasma, the opposing surface of at least one electrode of the pair should be provided with a solid dielectric, and the pair of electrodes may oppose to each other with a proper distance between them so as not to reach short-circuit, or they may be orthogonal.

[0047] The above-described solid dielectric is set on one of or both of the opposing surfaces of electrodes. At this time, the solid dielectric and the electrode of the side which is grounded are attached firmly to each other, and the opposing surface of the

electrode having contact is perfectly covered. When there is some part that is not covered with the solid dielectric so that the electrodes oppose to each other directly, an arc discharge easily occurs from there.

[0048] The shape of the above-described solid dielectric may be sheet-like, or film-like, and the thickness is preferably in a range of 0.01 to 4 mm. When it is too thick, sometimes a high voltage is required to generate plasma, and when it is too thin, a dielectric breakdown occurs when a voltage is applied and sometimes an arc discharge is generated. In addition, as the shape of the solid dielectric, a vessel-type one may be also used.

[0049] As the material of the solid dielectric, for example, plastic such as polytetrafluoroethylene and polyethylene terephthalate, glass, metal oxide such as silicon dioxide, aluminum oxide, zirconium dioxide and titanium dioxide, double oxide such as barium titanate, and the like can be used.

[0050] Especially, when a solid dielectric whose relative dielectric constant in a 25 °C environment is 10 or more is used, high-density discharge plasma can be generated by a low voltage, and the treatment efficiency improves. Although the upper limit of the relative dielectric constant is not limited specially, in actual materials, approximately 18,500 are available and can be used for the invention. A solid dielectric with the relative dielectric constant of in a range of 10 to 100 is especially preferable. Metal oxide such as zirconium dioxide and titanium dioxide, double oxide such as barium titanate can be cited as specific examples of the above-described solid dielectric with the relative dielectric constant of 10 or more.

[0051] The distance between electrodes described above is decided arbitrarily, considering the thickness of the solid dielectric, the size of the voltage applied, object of using plasma and the like, and it is preferably in a range of 1 to 50 mm. When it is less than 1 mm, it is not enough for setting the electrodes with a space between. On the other hand, when it is over 50 mm, it is difficult to generate uniform discharge plasma.

[0052] The above-described opposing electrodes provided with the solid dielectric does not have to be a pair, and a plurality of electrodes may be placed opposing to each other so that a plurality of discharge spaces are provided. By providing a plurality of discharge spaces, plasma of a large volumetric treatment gas can be generated, and a high-speed treatment can be performed.

[0053] In order to perform a uniform discharge, it is preferable that the surface roughness of the surface of the above-described solid dielectric, or the surface of the electrode in the case where the electrode is not covered with a solid dielectric and exposed to the discharge space side, is 10 μm or less. Therefore, the surfaces of the

solid dielectric or the electrode are preferably polished.

[0054] A pulsed electric field of the invention will be described. An example of a pulse voltage waveform is shown in Fig. 1. Waveforms (a) and (b) are an impulse type, a waveform (c) is a pulse type, and a waveform (d) is a modulation type. Although the voltage apply of repetitions of positive and negative is shown in Fig. 1, a pulse of the type in which a voltage is applied to either positive or negative polarity side may be used. Furthermore, a pulsed electric field where a direct current is superimposed may be applied. The waveform of a pulsed electric field of the invention is not limited to the ones described here, and modulation may be performed using pulses with different pulse waveforms, rise time and frequency. The above-described modulation is suitable for performing a high-speed continuous surface treatment.

[0055] The rise and/or fall time of the above-described pulsed electric field is preferably 10 μs or less. When it is over 10 μs, the discharge condition becomes unstable, easily changing into arc, and it becomes difficult to maintain a high-density plasma condition by a pulsed electric field. In addition, the shorter the rise time and the fall time are, the more efficiently ionization of the gas when plasma is generated occurs. However, it is practically difficult to realize a pulsed electric field whose rise time is less than 10 ns. More preferably, it is in a range of 10 ns to 5 μs. Here, rise time means the time when change in voltage is continuously positive, and fall time means the time when change in voltage is continuously negative.

[0056] Furthermore, the fall time of the pulsed electric field is preferably precipitous, and in the same way as the rise time, it is preferably a time scale of 10 μs or less. Although it differs depending on a pulsed electric field generation technique, the rise time and the fall time are preferably set as the same time.

[0057] The field intensity of the above-described pulsed electric field is preferably in a range of 10 to 1000 kV/cm. When the field intensity is less than 10 kV/cm, too much time is required for the treatment, and when it is over 1000 kV/cm, an arc discharge is easily generated.

[0058] The frequency of the above-described pulsed electric field is preferably in a range of 0.5 to 1000 kHz. When it is less than 0.5 kHz, too much time is required for the treatment since the plasma density is low, and when it is over 1000 kHz, an arc discharge is easily generated. More preferably, it is in a range of 1 to 100 kHz. By applying such a high-frequency pulsed electric field, the treatment speed can be greatly improved.

[0059] Furthermore, one pulse duration in the above-described pulsed electric field is preferably in a range of 0.5 to 200 μs. When it is less than 0.5 μs, the discharge is

unstable, and when it is over 200 μs, it becomes easy to change into an arc discharge. More preferably, it is in a range of 3 to 200 μs. Here, one pulse duration means a continuous ON time of one pulse in a pulsed electric field made of repetitions of ON and OFF, as shown with the example in Fig. 1.

[0060] In the invention, a means of bringing plasma into contact with a base material to be treated is leading the plasma generated between opposing electrodes toward the base material to be treated placed outside of the discharge space so as to have contact.

[0061] The method of the invention is a method in which the base material is hardly exposed to the high-density plasma space directly, and an electric and thermal burden to the base material is decreased. Especially, this method is excellent since it can treat a silicon wafer where an electric circuit is integrated with a plastic film whose melting point is low.

[0062] As specific methods, a method in which a solid dielectric is extended to form a plasma inducing nozzle, and plasma is sprayed toward a base material to be treated placed outside the discharge space, and the like can be cited as the example, and combinations of a parallel plate electrode and a long nozzle, a coaxial cylindrical electrode and a cylindrical nozzle can be used. The combination of a parallel plate electrode and a long nozzle is preferable since it can perform a large-area treatment. The material of the nozzle does not have to be the above-described solid dielectric, and it can be metal or the like as long as insulation from the above-described electrode is made.

[0063] Furthermore, with low pressure plasma, a discharge is easily spread. Therefore, it is preferable to provide a guide roughly vertically from a plasma outlet of plasma generated by the opposing electrodes toward a base material to be treated so as to lead the plasma to the objective place of the base material to be treated. By this guide, diffusion of plasma can be prevented.

[0064] Considering of treating a large-area base material, a gas outlet at the edge of the above-described nozzle is preferably 50 mm or more. In addition, in order to use the generated plasma efficiently, it is better that a distance between the discharge space and the gas outlet is short, so it is preferable that the electrode is along the shape of the gas outlet and 50 mm or more. Specifically, (a) parallel plate electrodes, having a long side, (b) a combination of a roll electrode and a roll electrode, (c) a combination of a roll electrode and a plate-like electrode, and (d) a combination of a roll electrode and a curved electrode are preferable. Cross-sectional views (the surface that is vertical to the long side direction) of the above-described electrodes are shown in Fig. 2. In order to perform a treatment of large area at high speed by using such electrodes, electrodes

with a size wherein the long side direction is bigger than the base material are used, and the base material or the electrodes are moved in the vertical direction to the long side so as to perform the treatment. A pulsed electric field is used in the invention, so it is possible to continue a stable discharge even with the electrode size over 50 mm as described above, and a uniform treatment can be performed all over the base material surface. In addition, to perform a uniform treatment, the gas is preferably uniform over the long side direction when passing through the electrodes.

[0065] The method of the invention can be used for multi chambers. That is, plasma devices with different gases and treatment conditions are arranged in the transporting direction, and film formation, etching and a cleaning treatment are performed in each device, so that these processes can be performed in block continuously. In the multi chamber device, the plasma treatment method of the invention and the other method may be combined. Furthermore, a treatment speed can be raised by using a multistage device made of a plurality of groups of electrodes, and a film stack can be formed by introducing different gases in each stage. In addition, the contact treatment of the invention is not limited to multistage processing of one surface of a base material to be treated by using a plurality of opposing electrodes that generate plasma, but the treatment can be performed from the both surfaces also. Generally, the discharge condition for atmospheric pressure plasma is narrow and the range affected by plasma is limited, so that the treatment can be easily prevented from going round to the rear surface, and also, different plasma treatments can be performed for the front and rear surfaces simultaneously by remote sources discharging different plasma. Especially, by changing the treatment gases flowing between the opposing electrodes, the front and rear surfaces both can be treated simultaneously by plasma based on different gases.

[0066] The method of the invention and a method in which plasma is brought into contact with a base material placed inside the discharge space of the plasma generated between opposing electrodes can be combined and used together.

[0067] The plasma treatment of the invention is characterized by its capability of performing the treatment at low temperature, especially at a temperature of 120 °C or less, compared to a conventional high temperature treatment. By performing the treatment at such a low temperature, this method can be applied to a base material that is sensitive to specially a thermal damage or the like. In addition, it is possible that a cooling mechanism or the like is added to a transporting means or the like which transports electrodes and base materials so that the temperature is controlled. In addition, in some treatments, the treatment can be performed at high temperature using a heating mechanism. The method of the invention can perform a stable treatment at

high temperature also.

[0068] Furthermore, in the plasma treatment of the invention, the treatment can be performed making an inert gas atmosphere in the vicinity of a contact part of plasma and a base material, in order to prevent the base material surface from being oxidized or prevent the base material surface after the treatment from contacting damp air or other impurities in the atmosphere.

[0069] As a mechanism for keeping an inert gas atmosphere in the vicinity of the contact part of plasma and the base material, a gas curtain mechanism by an inert gas, a mechanism for performing the treatment in a vessel filled with an inert gas, and the like can be cited as the examples.

[0070] As the gas curtain mechanism by an inert gas described above, a gas exhaust mechanism is provided around the vicinity of the contact part of plasma and the base material, and the gas curtain mechanism by an inert gas is provided around that, so that the vicinity of the contact part of plasma and the base material can be kept in the inert gas atmosphere.

[0071] Furthermore, in the device of the invention, a plasma generation mechanism having a nozzle body standby mechanism which moves a gas outlet nozzle to over a base material surface after a preliminary discharge is performed from the start of applying a voltage to electrodes until a discharge condition becomes stable can be used so that defectives are prevented from being produced.

[0072] Furthermore, as a means of transporting a base material, a transporting system made of a supply roll and a take-up roll can be used in the case where the base material is film-like, and transporting system such as a transporting conveyer and a transporting robot can be used in the case where the base material is sheet-like.

[0073] A specific device example of the invention will be described with drawings hereinafter. Fig. 3 is a diagram showing each example of a device which sprays a plasma gas on a base material to be treated by a parallel plate long nozzle, a device with a gas aspiration port provided around a gas outlet nozzle, and a device with a transport mechanism of the substance to be treated. Numeral 1 is a power supply, 2 and 3 are electrodes, 4 is a solid dielectric, 5 is a gas outlet, 7 is a treatment gas introducing port, 42 is a transporting belt, 9 is a discharge space, 10 is an exhaust gas tube, and 14 is a base material to be treated, respectively. For example, the treatment gas is introduced from the gas introducing port 7 to the discharge space 9 in the direction of an arrow, and spurted as plasma from the gas outlet 5 by applying a pulsed electric field between the electrode 2 and the electrode 3. On the other hand, the base material to be treated 14 is carried to the vicinity of the gas outlet by the belt 42, so as to be treated. The gas after

the treatment is removed from the exhaust gas tube 10, so that it does not attach to the base material to be treated again and contaminate. As for the transporting belt 42, by using one whose feed speed can be controlled arbitrarily, degree of the treatment can be changed, and furthermore, a cooling or heating mechanism can be added. In addition, according to need, the nozzle body as a whole can be provided with a nozzle standby mechanism which stands by outside the substance to be treated after a voltage is applied between the electrodes and a preliminary discharge is performed until the plasma becomes stable, and also it can be provided with an X-Y-Z transfer mechanism so as to be swept over the base material to be treated.

[0074] As for the above-described exhaust gas mechanism, it can be set so as to exhaust vertically to the gas blowing direction around the base material, or it can be set so as to exhaust from opposite side of the base material surface treated, besides setting in the vicinity of the outlet in the same direction as the gas blowing direction, as shown in Fig. 3.

[0075] Fig. 4 is a diagram showing each example of a device which sprays plasma on a base material using a cylindrical solid dielectric with a gas outlet, a device with a torus-shaped gas outlet provided around a gas outlet nozzle, and a transport mechanism of the base material. Numeral 1 is a power supply, 2 is an outside electrode, 3 is an inside electrode, 4 is a solid dielectric, 5 is a gas outlet, 7 is a treatment gas introducing port, 10 is an exhaust gas tube, 14 is a base material to be treated, and 41 to 43 are transporting belts, respectively. For example, the treatment gas is introduced from the gas introducing port 7 into a cylindrical solid dielectric vessel in the direction of an outline arrow, and spurted as plasma from the gas outlet 5 by applying a pulsed electric field between the electrode 2 placed outside the cylindrical solid dielectric vessel and the inside electrode 3 placed inside the cylindrical solid dielectric vessel. On the other hand, the base material to be treated 14 is carried by the transporting belt 41 first, then carried to the gas outlet by the transporting belt 42 next so as to be treated there, and after that, carried out by the transporting belt 43, which makes the transporting process. The gas after the treatment is removed from the exhaust gas tube 10, so that it does not attach to the base material again and contaminate. As for the transporting belts, by using ones whose feed speed can be controlled arbitrarily, degree of the treatment can be changed, and furthermore, a cooling or heating mechanism can be added. In addition, according to need, the nozzle body formed of a cylindrical solid dielectric can be provided with a nozzle standby mechanism which stands by outside the base material after a voltage is applied between the electrodes and a preliminary discharge is performed until the plasma becomes stable, and also it can be provided with an X-Y-Z

transfer mechanism so as to be swept over the base material.

[0076] Fig. 5 is a diagram to describe an example of a method for treating a base material to be treated by a device structured by a nozzle body having a plurality of discharge spaces due to a plurality of plate electrodes. Numeral 1 is a power supply, 2 and 3 are electrodes, 5 is a gas outlet, 7 is a treatment gas introducing port, 14 is a base material to be treated, and 41 to 43 are transporting belts, respectively. Although not shown in the figure, the electrodes are coated with a solid dielectric. For example, the treatment gas is introduced from the gas introducing port 7 into the nozzle body having a plurality of discharge spaces in the direction of an outline arrow, and spurted as plasma from the gas outlet 5 by applying a pulsed electric field between the electrode 2 and the electrode 3. On the other hand, the base material to be treated 14 is carried by the transporting belt 41 first, then carried to the gas outlet by the transporting belt 42 next so as to be treated there, and after that, carried out by the transporting belt 43, which makes the transporting process. In this device, the number of discharge spaces can be large, which is preferable for a treatment of a large-area base material to be treated.

[0077] Fig. 6 is a perspective view describing a nozzle body using roll electrodes. In order to describe inside of the nozzle body, a part of outside casing is shown with a dotted line. Fig. 7 is a longitudinal cross-sectional view of Fig. 6. In Fig. 6 and Fig. 7, numeral 1 is a power supply, 2 is a ground roll electrode, 3 is an applied roll electrode, 4 is a solid dielectric, 5 is a plasma outlet, 7 is a treatment gas introducing port, 30 is a casing, 31 is a swash plate, 32 is a perforated plate, and 33 is a treatment gas circulation hole, respectively.

[0078] The treatment gas is introduced from the gas introducing port 7 in the direction of an outline arrow, and the flow rate is made uniform in the length direction by the swash plate 31 and the perforated plate 32. Then, by a pulsed electric field applied between the roll electrodes, it is spurted as plasma from the plasma outlet 5, and sprayed on a base material to be treated placed in the vicinity. In this device, the nozzle body can be provided with an X-Y-Z transfer mechanism so that the base material is swept, and a large-area base material can be treated in a short period of time.

[0079] Furthermore, as for the nozzle body of the invention, by moving the gas outlet nozzle to the base material surface after a preliminary discharge is performed from the start of applying a voltage to the electrodes until the discharge condition becomes stable, defectives are prevented from being produced. The contour of the device is shown in Fig. 8.

[0080] Fig. 8 is a diagram describing an example of using a plasma generation

mechanism having a nozzle body standby mechanism. It is a device that introduces a treatment gas to a nozzle body 6 and sprays plasma on a base material 14. The nozzle body 6 stands by at a position A at the time of a preliminary discharge until the discharge condition becomes stable, and after the discharge condition becomes stable, it is moved to a position B where a nitride film is to be formed on the surface of the base material 14 and deposition of the nitride film is started. In addition, in this device, exhaust of the treatment gas can be performed by providing a ring-shaped hood 10 which surrounds a support 15. Furthermore, by providing a transporting robot 20 together, the base material 14 is taken in and out from a cassette 21, and a treatment of the base material can be performed effectively. The above-described nozzle body standby mechanism can be used with an X-Y-Z transfer mechanism to sweep the nozzle body. In addition, it can be put in a vessel filled with an inert gas.

[0081] Furthermore, an example of a device to treat a sheet-like base material is shown in Fig. 9. In a vessel 30 provided with a gas introducing port 7 and a gas outlet 5, a solid electrode is placed on an opposing surface of at least one of opposing electrodes 2 and 3, and a material gas excited between one of the electrodes and the solid dielectric, or between the pair of solid dielectrics, is sprayed continuously from the gas outlet 5 in an arrow direction on a surface of a sheet-like or film-like base material 14 which is moving by a roll, so that a thin film 16 is formed on the base material.

[0082] Furthermore, an example of a device with a pair of parallel plate electrodes and a pair of cylindrical electrodes combined is shown in Fig. 10. In a vessel 30 provided with a gas introducing port 7 and a gas outlet 5, there are a pair of parallel plate electrodes made of electrodes 2 and 3, and a pair of cylindrical electrodes made of electrodes 2’ and 3’. Furthermore, on an edge of the gas outlet 5, a guide 6’ is provided roughly vertically toward a base material to be treated 14. A material gas is excited between each pair of electrodes and generates plasma, and more uniform plasma can be generated by rotating the cylindrical electrodes, and furthermore, the plasma can be concentrated on the surface of the base material 14 by the guide 6.

[0083] With the atmospheric pressure discharge using a pulsed electric field of the invention, it is possible to generate a discharge directly under an atmospheric pressure between electrodes, not depending on the gas kind at all, and a high-speed treatment can be realized by the atmospheric pressure plasma device with the more simplified electrode structure and discharge procedure, and by the treatment method. In addition, by parameters of the pulse frequency, voltage, distance between electrodes and the like, parameters for the treatment can be controlled.

[0084] The treatment method of the invention can be used for CVD film formation of

an oxide film used as an insulating film, a passivation film, an optical film or the like, an EL film used for light emission, a nitride film used as an insulating film and a passivation film, a metal film used as a wiring and a catalyst for a fuel cell, DLC used for passivation, adding smoothness and anticorrosion coating, a transparent conductive film used as an electrode on a glass substrate and a plastic substrate, a low-k film used as a high-frequency insulating film, a high-k film used for a high-density memory and a piezoelectric element, a poly-Si film used for TFT (LSI on a glass substrate), an a-Si:H film used for a solar cell and the like.

[0085] Furthermore, it can also be used effectively for an ashing treatment of a photoresist, a discame or the like, an isotropic or anisotropic etching treatment, a cleaning treatment such as an oxide film removal and an organic pollutant removal, an oxidation process, a doping process, after coating process and the like, in a semiconductor process and a manufacturing process of an electronic component.

[0086]

[Embodiments] The invention will be described in more detail, based on embodiments, but the invention is not limited only to these embodiments.

[0087] Embodiment 1

Using parallel plate electrodes of 200×50×8 mm whose surfaces are coated with alumina of 0.5 mm thick manufactured by SUS, using the device of Fig. 3 with the distance between the electrodes 2mm, using a circuit substrate as a base material to be treated, and introducing a mixed gas of oxygen 25 volume % and an argon gas 75 volume % at 10L/min as a treatment gas, a surface cleaning treatment of the circuit substrate is performed under the following conditions.

[0088] Discharge condition: waveform (a), rise/fall time 5μs, Vp-p 12kV, frequency 10 KHz, treatment time 30 sec.

[0089] The plasma generated is a uniform discharge condition without streamer, and the electrode temperature during the treatment is 60 °C, the substrate temperature is 40 °C, which are the highest values for each. When an operation test of the circuit substrate after the treatment is conducted, it operates normally. When abundance of carbon on the surface of the circuit substrate before and after the treatment is checked by ESCA, before the treatment is 62 atom %, and after the treatment is 5 atom %, which verifies the superior cleaning capacity.

[0090] Embodiment 2

Setting the treatment gas a drying air 20 L/min, Vp-p 20 kV, and other conditions the same as Embodiment 1, a surface cleaning treatment of a circuit substrate is performed. A uniform plasma condition without streamer is obtained, and the electrode temperature

during the treatment is 60 °C, the substrate temperature is 40 °C, which are the highest values for each. When an operation test of the circuit substrate after the treatment is conducted, it operates normally. When abundance of carbon on the surface of the circuit substrate before and after the treatment is checked by ESCA, before the treatment is 62 atom %, and after the treatment is 4 atom %, which verifies the superior cleaning capacity.

[0091] Comparative Example 1

Applying a high-frequency voltage of 13.56 MHz and 250 W between the electrodes, and setting other conditions the same as Embodiment 1, a surface cleaning treatment of a circuit substrate is performed. A streamer discharge is observed, and the electrode temperature rises over 200 °C. It is dangerous to continue the treatment, so the treatment is stopped in 5 sec after applying a voltage. When an operation test of the circuit substrate after the treatment is conducted, it does not operate. It is considered that short circuit occurred because of a thermal damage.

[0092] Comparative Example 2

Applying a high-frequency voltage of 13.56 MHz and 250 W between the electrodes, using a mixed gas of helium 45 volume %, argon 45 volume %, and oxygen 10 volume % as a treatment gas, and setting other conditions the same as Embodiment 1, a surface cleaning treatment of a circuit substrate is performed. The electrode temperature is kept at 200 °C or less, using a cooling mechanism. A streamer discharge is observed, and it is dangerous to continue the treatment, so the treatment is stopped in 10 sec after applying a voltage. Then, changing the treatment gas to a mixed gas of helium 90 volume % and oxygen 10 volume %, the treatment is performed for 30 sec. The substrate temperature becomes 150 °C. When an operation test of the circuit substrate after the treatment is conducted, it does not operate. It is considered that short circuit occurred because of a thermal damage. When abundance of carbon on the surface of the circuit substrate before and after the treatment is checked by ESCA, before the treatment is 62 atom %, and after the treatment is 46 atom %.

[0093] Embodiment 3

The device of Fig. 10 is set to have parallel plate electrodes of 200×50×8 mm whose surfaces are coated with alumina of 0.5 mm thick manufactured by SUS (the distance between the electrodes 2 mm) and roll electrodes of diameter 25 mm whose surfaces are coated with alumina of 0.5 mm thick manufactured by SUS (the distance between the electrodes 2 mm), and a gas guide of 3 mm long toward just below the roll part is put so that the side is blocked and only the leading edge is opened. A glass substrate is placed 1 mm away from the nozzle, as a base material to be treated. Flowing CF_4 100

% as a treatment gas with the flow rate of 1 SLM, and applying discharge output 500 W and frequency 10 kHz to the electrodes, the base material is etched for 5 min. After the etching, when the etching depth on the base material surface is measured by a probe-type profilometer, it is etched to a depth of 0.5 μ anistropically. Furthermore, characteristic luminescent color of orange is seen in the discharge part.

[0094]

[Effect of the Invention] An atmospheric pressure plasma treatment method of the invention is a treatment method using a simple device structure which can deal with a high speed treatment and a large-area treatment, and does not thermally or electrically damage a base material to be treated, therefore, it can be used effectively for all plasma treatment methods starting with various methods used in a semiconductor manufacturing process, to realize inlining and higher speed. By this, the treatment time can be shortened, the cost can be reduced, and expansion to various uses which used to be impossible or difficult conventionally becomes possible.

[Brief Description of the Drawings]

Fig. 1 is a diagram of a voltage waveform showing an example of a pulsed electric field of the invention.

Fig. 2 is diagrams to describe combinations of electrode shapes of the invention.

Fig. 3 is a diagram to show an example of a discharge plasma treatment device of the invention.

Fig. 4 is a diagram to show an example of a discharge plasma treatment device of the invention.

Fig. 5 is a diagram to show an example of a discharge plasma treatment device of the invention.

Fig. 6 is a diagram to show an example of a nozzle body of the invention.

Fig. 7 is a longitudinal cross-sectional view of Fig. 6.

Fig. 8 is a diagram to show an example of a discharge plasma treatment device of the invention.

Fig. 9 is a diagram to show an example of a discharge plasma treatment device of the invention.

Fig. 10 is a diagram to show an example of a discharge plasma treatment device of the invention.

[Description of Symbols]

1: power supply (high voltage pulsed power supply)

2, 2’, 3 and 3’: electrode

4: solid dielectric
5: gas outlet
6: nozzle body
6': guard
7: gas introducing port
9: discharge space
10: gas exhaust tube
14: base material to be treated
15: support
16: thin film
20: transporting robot
21: cassette
22: arm
30: casing
31: swash plate
32: perforated plate
33: treatment gas circulation hole
41, 42 and 43: transporting belt

Continued from the front page
(51) Int. Cl.^{7}: H05H 1/46
Identification Mark
FI: H01L 21/302
Theme Code (reference): N
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F Term (reference): 4G075, AA24, AA30, BC04, BC06, BC07
BC10, CA47, CA62, CA63, DA18
EB41, EB42, EB43, EC01, EC21
EE01, EE02, EE12, FB01, FB02
FB06, FB12, FC15
5F004, AA14, BA04, BB11, BB29, BD01
BD04, DA23, DA26
5F045, AA08, AB03, AB04, AB33, AB34
AE29, DP22, EH08, EH13

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報**（Ａ）　(11)特許出願公開番号
特開2002－237480
（P2002－237480A）
(43)公開日　平成14年8月23日(2002.8.23)

(51)Int.Cl.⁷	識別記号	ＦＩ	テーマコード（参考）
Ｈ０１Ｌ　21/304	６４５	Ｈ０１Ｌ　21/304	６４５Ｃ　４Ｇ０７５
Ｂ０１Ｊ　19/08		Ｂ０１Ｊ　19/08	Ｈ　５Ｆ００４
Ｈ０１Ｌ　21/205		Ｈ０１Ｌ　21/205	５Ｆ０４５
21/3065		Ｈ０５Ｈ　1/26	
Ｈ０５Ｈ　1/26		1/46	Ｍ

審査請求　未請求　請求項の数14　ＯＬ　（全 12 頁）
最終頁に続く

(21)出願番号　特願2001－200835(P2001－200835)
(22)出願日　平成13年7月2日(2001.7.2)
(31)優先権主張番号　特願2000－229322(P2000－229322)
(32)優先日　平成12年7月28日(2000.7.28)
(33)優先権主張国　日本（ＪＰ）
(31)優先権主張番号　特願2000－369489(P2000－369489)
(32)優先日　平成12年12月5日(2000.12.5)
(33)優先権主張国　日本（ＪＰ）

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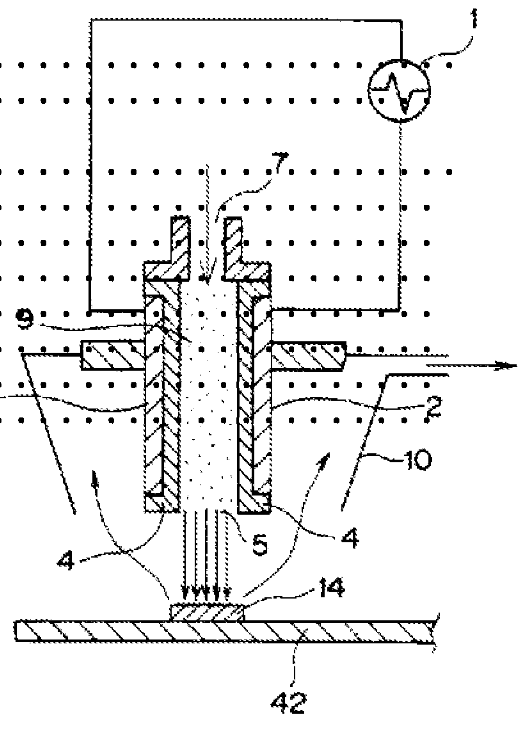
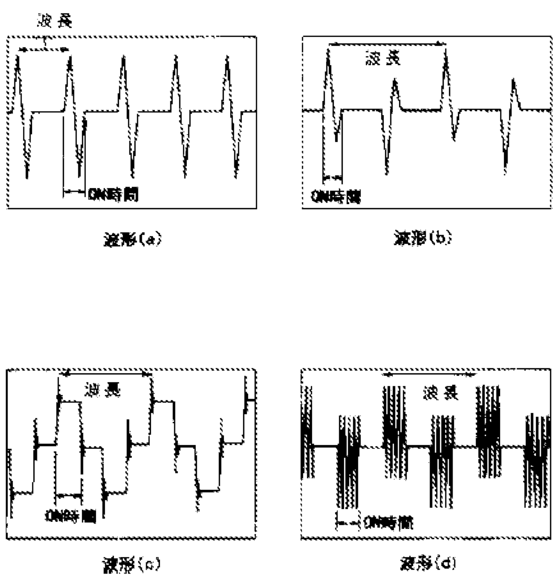
(54)【発明の名称】　放電プラズマ処理方法

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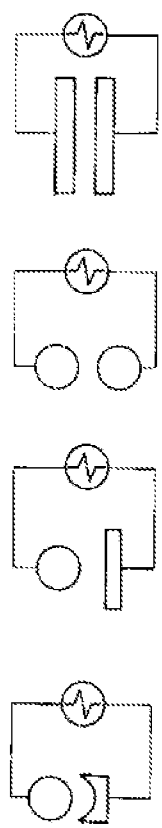

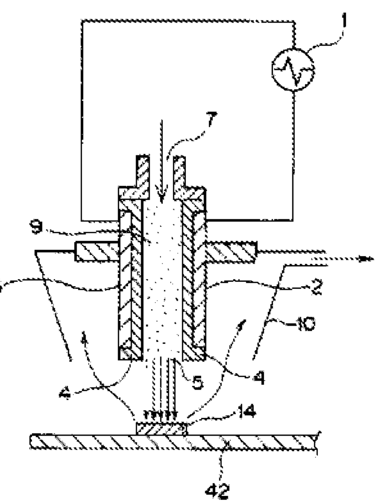
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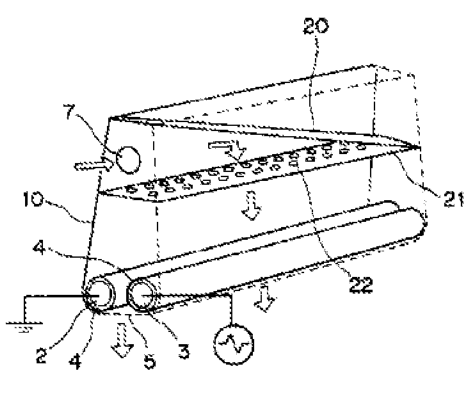
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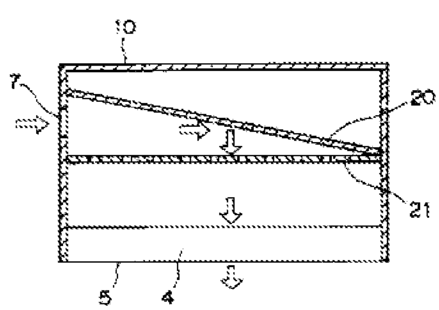
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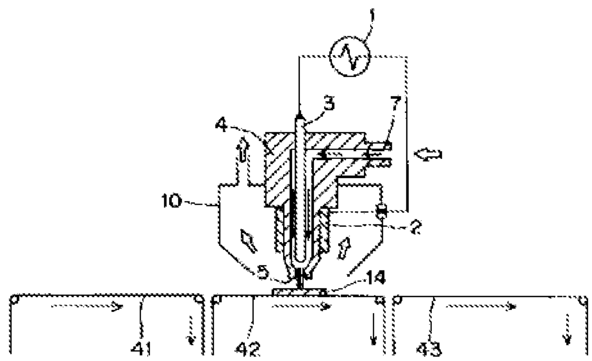
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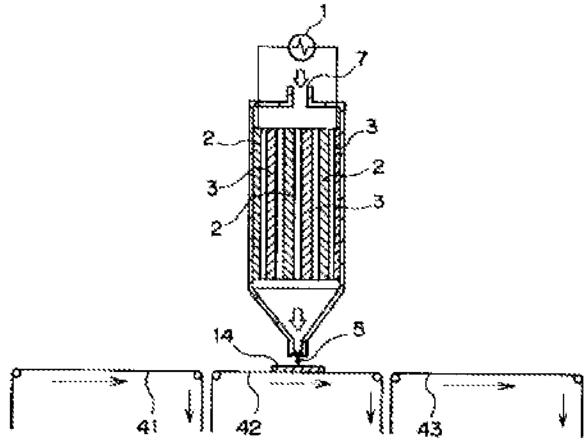
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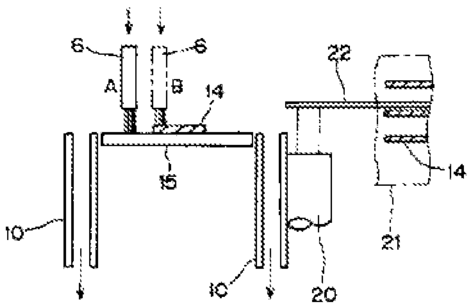
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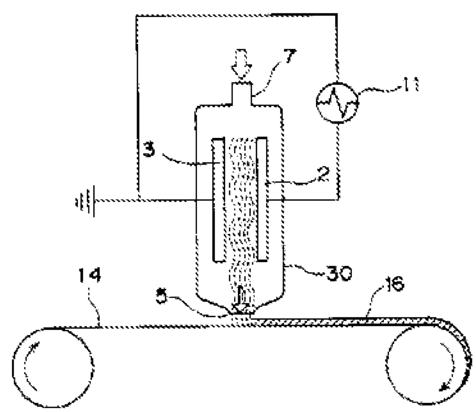
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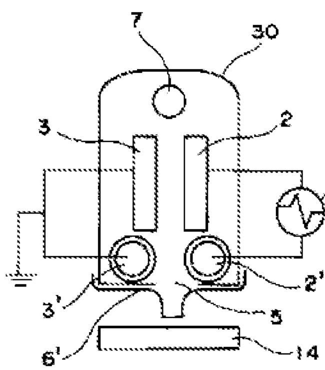
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